Do Large-scale Remedial and Dredging Events Have the Potential to Release Significant Amounts of Semivolatile Compounds to the Atmosphere?

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Laboratory studies suggest that substantial amounts of polychlorinated biphenyls are rapidly volatilized from wet contaminated solids during water evaporation. If significant losses also occur during field activities, potential analytical, global, and health implications should be considered in the design and monitoring of remedial actions and the handling of contaminated solids. *Key words:* dredging, *ortho*-substituted congeners, polychlorinated biphenyls, semivolatile compounds, volatilization. *Environ Health Perspect* 106:47–49 (1998). [Online 21 January 1998]
http://ehpnet1.niehs.nih.gov/docs/1998/106p47-49chiarenzelli/abstract.html

Recent experiments monitoring the loss of polychlorinated biphenyls (PCBs) from wet sediment (*1,2*) and subaqueous sand (*3*) have shown that a strong correlation exists between water evaporation and PCB volatile loss, implying that PCBs can be released during drying of contaminated solids. Similar relationships between the volatile loss of dibenzofuran, phenanthrene, and pyrene from dredged sediment and the relative humidity of air have also recently been described (*4*). While these findings are somewhat surprising if viewed from the perspective of the perceived relative immobility of hydrophobic semivolatile compounds like PCBs, it has long been recognized that the volatile loss of chlorinated pesticides from soil is considerably enhanced by moisture (*5*). This phenomena, termed wicking in early studies, is related to competition between water molecules and contaminants for absorption sites on mineral surfaces (*6*). PCB volatilization is enhanced by environmental transformations of parent compounds yielding more soluble and volatile congeners. In this commentary we briefly summarize the salient points of this research, discuss PCB physicochemistry and volatilization, and speculate briefly on the significance of these findings in terms of potential analytical, remedial, global, and health implications.

Volatile Loss of PCBs from Wet Sediment

The volatilization of PCBs from soils (*7*) and large contaminated water bodies (*8*) has been extensively investigated and is thought to be a major pathway by which PCBs and pesticides are lost from these reservoirs (*9*) and are globally distributed. However, there is little research available in the peer-reviewed literature on the volatile loss of PCBs from sediment (*10*), despite the findings of U.S. Army Corp of Engineers-sponsored investigations (*11–13*). A fortuitous discovery in our laboratory of PCB volatile losses of ~75% (n = 4) during evaporation of water from small amounts of anaerobically dechlorinated St. Lawrence River sediment during a period of 1 week prompted additional investigations of this phenomenon (*1–3*). Subsequent controlled replications of this experiment yielded similar results [73.4 ± 1.5% (mean ± standard deviation); n = 3]. Experiments designed to investigate losses over shorter time periods (24 hr; 18.0 ± 3.2% loss; n = 9) and with variable initial moisture content were subsequently conducted and were strongly correlated with water evaporation. The volatilized fractions recovered in all experiments were predominantly lower *ortho*-chlorinated congeners (2, 2/2, 2/6, 26/2; IUPAC numbers 1, 4, 10, 19). In experiments of shorter duration (24 hr) and with lower initial moisture contents (35–50%), 80–90% of the PCB volatile loss occurred within the first 8 hr and ended when the sediment dried. In experiments with variable moisture content, an exponential increase in PCB volatilization was noted for moisture contents above 26% relative humidity, equivalent to a monolayer coating of water molecules (*6*). Additional PCBs were volatilized when dried sediment was remoistened.

Physicochemical Properties and Environmental Changes

Significant progress in the understanding of how PCBs partition in the environment and impact organisms has been made in the last decade. Much of this can be attributed to the development and use of analytical techniques capable of measuring individual PCB compounds (congener-specific capillary column gas chromatography). Accurate information on how PCBs and other similar organochlorine compounds partition and degrade in the environment is essential to determine their ultimate fate and ecosystem impact and, consequentially, to arrive at informed remedial decisions. Contrary to widely held notions of their chemical stability and immobility, PCBs are now known to undergo alteration, partitioning, and degradation in certain environmental systems. Although these concepts are appreciated by PCB researchers, they are yet to be fully recognized by the scientific community at large or integrated into regulatory policy considerations.

The degree of chlorination of PCBs determines their physicochemical properties, such as solubility, octanol–water partitioning coefficients, and Henry's Law constants, and thus their mobility (*14*). Anaerobic microbial degradation, resulting in partial dechlorination of PCB congeners, has now been reported from numerous localities (*15*) including the St. Lawrence (*16*) and Hudson (*17*) Rivers. Although dechlorination is widely inferred to be environmentally beneficial, these transformations result in the production of more mobile and bioavailable daughter products and increase the potential for transport by water or air. Large concentrations of microbial dechlorination daughter products with one to three chlorines have been measured in sediments from the St. Lawrence and Hudson Rivers. Three of these (2, 2/2, 2/6) comprise over 65% of the PCBs transported by waters of the upper Hudson River (*18*). In contrast to the more highly chlorinated PCB congeners with solubilities below the part-per-billion range, these congeners are soluble at the part-per-million level and have the highest Henry's Law constants (*19*).

Possible Implications

These measurements of PCB volatility from biodegraded sediment, although based on small-scale experiments, may have implications for the handling of PCB-contaminated media. From an analytical perspective, significant changes can be expected as environmental media are allowed to air dry or evaporate,

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The authors wish to acknowledge funding from the New York Sea grant Institute (grant SG-94-061) and from the National Institute for Environmental Health Sciences Basic Research Program (grant P42 ES04913). The authors also appreciate the helpful comments of the reviewers.
Received 9 June 1997; accepted 8 October 1997.

even for short periods. Anticipated changes include lowering of total concentrations and alteration of relative congener abundances. These alterations can mask environmental transformations; result in erroneous assumptions of aerobic biodegradation (e.g., disappearance of *ortho*-chlorinated PCB congeners); impose bias on retrospective studies of archived samples; confuse fingerprinting of contaminant sources; or, because of reduced concentrations, reduce liability or result in improper disposal.

Of greater concern, however, is the potential volatile losses of semivolatiles during large-scale remedial, dredging, land farming operations involving contaminated solids and the use of contaminated sediments for fill or landfill cover material. In particular, PCB mixtures with a high proportion of more mobile congeners, including those produced by microbial degradation or originally present in less chlorinated Aroclors (e.g., 1016, 1242, 1248), have the potential to lose significant quantities of PCBs during handling and drying.

Within New York State, a number of large-scale dredging projects involving contaminated sediments are under consideration. In the St. Lawrence River, over 100,000 yd^3 of sediment contaminated with PCBs (Aroclor 1248) and polycyclic aromatic hydrocarbons (PAHs) have been dredged, and additional dredging is required. Dredging of the upper Hudson River, which has been debated for two decades in relation to industrial discharges of 2,000–4,500 metric tons of Aroclor 1242 (*20*), could occur in the future. The PCB fractions of sediments from both the St. Lawrence and Hudson rivers are dominated by lower chlorinated congeners (*16,21*) derived from both microbial dechlorination and the original Aroclor composition. A dredging project, prompted by navigational needs and dwarfing either of these actions, is planned for the New York–New Jersey Harbor area and will involve removal, transportation, and disposal of approximately $4–5 \times 10^6$ m^3/year of sediment for 5 years. A large portion of this sediment is contaminated with a wide variety of semivolatile compounds including PCBs, PAHs, dioxins, and pesticides. Volatile losses of contaminants during staging, dewatering, drying, transportation, or upland of or at contained disposal facilities are likely and cannot be reliably estimated from the existing database (*4*).

Land farming, an increasingly popular treatment method for contaminated soil or sediment, also has the potential to release significant quantities of contaminants via volatilization. Temporal contaminant reductions in many land farming operations have been attributed to bioremediation with little or no evaluation of volatile losses, despite a considerable body of literature showing positive relationships between pesticide loss and soil temperature, moisture content, or precipitation events (*5*). In addition, many *in situ* bioremediation efforts employ the injection of air or oxygen, or vapor stripping to enhance microbial activity. Little is known of the magnitude of volatile losses during these activities.

The volatile loss of PCBs and other semivolatile organic pollutants from soil, sediment, and water is the primary pathway responsible for their global redistribution. Global fractionation theories propose that the more mobile congeners of various contaminant classes (e.g., PCBs, PAHs, polychlorinated dibenzodioxins and dibenzofurans, chlorobenzenes, chlorinated pesticides) preferentially volatilize, migrate, condense, and fall out in polar regions (*22,23*), consistent with their physicochemical properties (*14*). The flux, ultimate fate, and potential impact of these contaminants in polar regions is largely unknown.

Long documented to be carcinogenic, PCBs are now implicated in other human health effects, including permanent reduction in IQ and altered behavior in developing fetuses and children exposed to the mother's contaminant body burden *in utero* (*24*). There is significant evidence from animal studies implicating *ortho*-substituted, lower chlorinated congeners in these neurotoxic effects (*25–28*). Given the potential for volatile releases dominated by *ortho*-substituted, lower chlorinated congeners during sediment dredging or remedial operations, PCB exposure to local populations (*29*) warrants further investigation particularly via inhalation, which has been largely neglected since the initial studies carried out by the Halowax Corporation in 1936 (*30*). Although lower chlorinated PCB congeners are generally considered to be rapidly metabolized and excreted, they have been found in subpopulations of fetal cord blood and mother's milk samples from upstate New York (*31,32*), possibly implying continuous exposure through inhalation. Studies are needed to evaluate contaminant air concentrations and the significance of inhalation exposure to populations residing near activities likely to lead to volatile releases.

Summary

Contaminated solids (soil, sediment, sludge) represent significant repositories of PCBs and other semivolatile compounds with similar physicochemical properties currently isolated from circulation. Alteration of these sediments by microbial processes results in dechlorination and the production of more mobile and bioavailable daughter products. Experimental data suggest that lower chlorinated PCB congeners are highly susceptible to volatile loss during co-evaporation with water. By extrapolation, similar findings are anticipated for other classes of semivolatile compounds. Dredging, remedial, or land farming operations targeting large isolated or buried contaminant repositories may have the potential to release semivolatile compounds to the atmosphere. Studies of contaminant air concentrations associated with remedial activities and potential exposure via volatilization to local inhabitants are sorely needed, as are new guidelines to address sample analysis and handling. We urge that the volatility of semivolatile compounds be considered in decisions regarding possible remedial intervention, beneficial use, and in design and implementation of remedial activities.

References

1. Chiarenzelli J, Scrudato R, Arnold G, Wunderlich M, Rafferty D. Volatilization of polychlorinated biphenyls from sediment during drying at ambient conditions. Chemosphere 33:899–911 (1996).
2. Chiarenzelli J, Scrudato R, Wunderlich M, Oenga G, Lashko O. PCB volatile loss and the moisture content of sediment during drying. Chemosphere 34: 2429–2436 (1997).
3. Chiarenzelli J, Scrudato R, Wunderlich M. Volatile loss of PCB Aroclors from subaqueous sand. Environ Sci Technol 31:597–602 (1997).
4. Valsaraj K, Choy B, Ravikrishna R, Thibodeaux L, Price C, Brannon J, Myers T. Air emissions from exposed, contaminated sediments and dredged materials. 1. Experimental data in laboratory microcosms and mathematical modeling. J Hazard Materials 54:65–87 (1997).
5. Majewski M, Desjardins R, Rochette P, Pattey E, Seiber J, Glotfelty D. Field comparison of an eddy accumulation and an aerodynamic-gradient system for measuring pesticide volatilization fluxes. Environ Sci Technol 27:121–128 (1993).
6. Goss K. Effects of temperature and relative humidity on the sorption of organic vapors on quartz sand. Environ Sci Technol 26: 2287–2294 (1992).
7. Eduljee G. Volatilization of TCDD and PCB from soil. Chemosphere 16:907–920 (1987).
8. Achman D, Hornbuckle K, Eisenreich S. Volatilization of polychlorinated biphenyls from Green Bay, Lake Michigan. Environ Sci Technol 27:75–86 (1993).
9. Harrad S, Sewart A, Alcock R, Boumphrey R, Burnett V, Duarte-Davidson R, Halsall C, Sanders G, Waterhouse K, Wild S. Polychlor-inated biphenyls (PCBs) in the British environment: sinks, sources and temporal trends. Environ Pollut 85:131–146 (1994).
10. Larsson P. Contaminated sediments of lakes and oceans act as sources of chlorinated hydrocarbons for release to water and atmosphere. Nature 317:347–349 (1985).
11. Brannon J. Laboratory Assessment of Volatilization from New Bedford Harbor Sediment, Memorandum for Record. WESES-A. Vicksburg, MS:U.S. Army Engineer Waterways Experiment Station, 1989.
12. Thibodeaux L. Theoretical models for volatile emissions from dredged materials—comparison of predicted and laboratory measurements for New Bedford Harbor sediment, Memorandum for Record. Contract No. DACW39-89-M-0207. Vicksburg, MS:U.S. Army Engineer Waterways Experiment Station, 1989.
13. Palermo M, Miller J. Disposal alternatives for PCB-

contaminated sediments from Indiana Harbor, Indiana. Miscellaneous Paper EL-87-9. Vol I. Vicksburg, MS:U.S. Army Engineer Waterways Experiment Station, 1987.
14. Wania F, Mackay, D. Tracking the distribution of persistent organic pollutants. Environ Sci Technol 30:390A–396A (1996).
15. Spain J. Synthetic chemicals with potential for natural attenuation. Bioremediation J 1:1–9 (1997).
16. Sokol R, Kwon O-S, Bethoney C, Rhee G-Y. Reductive dechlorination of polychlorinated biphenyls in St. Lawrence River sediments and variations in dechlorination characteristics. Environ Sci Technol 28: 2054–2064 (1994).
17. Brown M, Bush B, Rhee G-Y, Shane L. PCB dechlorination in Hudson River sediments. Science 240:1674–1675 (1988).
18. Bush B, Simpson KW, Shane L, Koblintz RR. PCB congener analysis of water and caddisfly larvae (*Insecta*:*Trichoptera*) in the upper Hudson River by glass capillary chromatography. Bull Environ Contam Toxicol 34:96–105 (1985).
19. Brunner S, Hornung E, Santi H, Wolff E, Piringer O, Altschuh J, Brüggman R. Henry's Law constant for polychlorinated biphenyls: experimental determination and structure–property relationships. Environ Sci Technol 24:1751–1754 (1990).
20. Sanders J. PCB pollution in the upper Hudson River: from environmental disaster to "environmental gridlock." Northeast Environ Sci 8:1–87 (1989).
21. Bush B, Shane L, Whalen M, Brown M. Sedimentation of 74 PCB congeners in the upper Hudson river. Chemosphere 16:733–744 (1987).
22. Rappe C. In: Ecological Problems of the Circumpolar Area (Bylund E, Linderholm H, Rune O, eds). Luleå, Sweden:Norsbotten Museum, 1974;29–32.
23. Wania F, Mackay D. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. Ambio 22:10–18 (1993).
24. Jacobsen J, Jacobsen S. Intellectual impairment in children exposed to polychlorinated biphenyls in utero. N Engl J Med 335:783–789 (1996).
25. Shain W, Bush B, Seegal R. Neurotoxicity of polychlorinated biphenyls: structure–activity relationship of individual congeners. Toxicol Appl Pharmacol 111:33–42 (1991).
26. Maier W, Rao P, Kodavanti S, Harry G, Tilson H. Sensitivity of adenosine triphosphatases in different brain regions to polychlorinated biphenyl congeners. J Appl Toxicol 14:225–229 (1994).
27. Eriksson P, Fredriksson A. Developmental neurotoxicity of four *ortho*-substituted polychlorinated biphenyls in the neonatal mouse. Environ Toxicol Pharmacol 1:155–165 (1995).
28. Kodavanti P, Ward T, McKinney J, Tilson H. Inhibition of microsomal and mitochondrial Ca^{2+}- sequestration in rat cerebellum by polychlorinated biphenyl mixtures and congeners: structure–activity relationships. Arch Toxicol 70:150–157 (1996).
29. Cullen A, Vorhees D, Altshul L. Influence of harbor contamination on the level and composition of polychlorinated biphenyls in produce in greater New Bedford, Massachusetts. Environ Sci Technol 30:1581–1588 (1996).
30. Drinker C, Warren M, Bennet G. The problem of possible systemic effects from certain chlorinated hydrocarbons. J Ind Hyg Toxicol 19:283–299 (1937).
31. Bush B, Snow J, Koblintz R. Polychlorobiphenyl (PCB) congeners, *p-p*′-DDE and hexachlorobenzene in maternal and fetal cord blood from mothers in upstate New York. Arch Environ Contam Toxicol 13:517–527 (1984).
32. Bush B, Snow J, Connor S, Koblintz R. Polychlorinated biphenyl congeners, *p-p*′-DDE and hexachlorobenzene in human milk in three areas of upstate New York. Arch Environ Contam Toxicol 14:443–450 (1985).